

On the effects of the magnetic field and the isotopic substitution upon the infrared absorption of manganites

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(February 1, 2008)

Employing a variational approach that takes into account electron-phonon and magnetic interactions in $La_{1-x}A_xMnO_3$ perovskites with $0 < x < 0.5$, the effects of the magnetic field and the oxygen isotope substitution on the phase diagram, the electron-phonon correlation function and the infrared absorption at $x = 0.3$ are studied. The lattice displacements show a strong correlation with the conductivity and the magnetic properties of the system. Then the conductivity spectra are characterized by a marked sensitivity to the external parameters near the phase boundary.

The perovskite oxides $La_{1-x}A_xMnO_3$ (A represents a divalent alkali element such as Sr or Ca) exhibit the colossal magnetoresistance (CMR) effect within the hole doping range $0.2 \leq x \leq 0.5$.¹⁻³ These compounds are characterized by a transition from a metallic ferromagnetic (FM) low-temperature phase to an insulating paramagnetic (PI) high-temperature phase that is associated with dramatic changes in their electronic and magnetic properties.

These materials were first studied in the 1950's for their peculiar strong correlation between magnetization and resistivity.⁴ The ferromagnetic phase was explained by introducing the double exchange mechanism^{5,6} that takes into account the combined effect of the $Mn\ e_g$ electron hopping between nearest neighbor sites and the very strong Hund's exchange with the localized $Mn\ t_{2g}$ electron spins. Later on, in addition to the double-exchange physics, a strong interaction between electrons and lattice distortions has been suggested in order to explain the CMR phenomenon.⁷

At high temperatures, above the Curie temperature T_c , the Jahn-Teller polaron formation has been confirmed by many experimental measurements,⁸ in particular by the activated behavior of the conductivity,^{9,10} the thermopower,^{11,12} the Hall mobility¹³ and more directly by atomic pair distribution,¹⁴ electron paramagnetic resonance,¹⁵ x-ray and neutron scattering studies.¹⁶⁻¹⁸ X-ray-absorption fine-structure ($XAFS$) spectra have found significant changes in the local structure of these compounds showing the crossover from large to small polarons across the metal-insulator (MI) transition and the direct relationship between lattice distortions, charge distribution and magnetism.¹⁹⁻²³ Indeed the charge carriers partly retain their polaronic character even below T_c , as proved by neutron pair-distribution-function analysis²⁴ and resistivity measurements.²⁵ Pseudogap features^{26,27} and conductivity spectra²⁸⁻³¹ have also been discussed in terms of a strong coupling to lattice distortions. Finally the existence of the strong electron-phonon coupling and polarons has been demonstrated by the giant isotope shift of the Curie temperature.^{32,33} Nowadays the key-role of the polaron formation in manganites is generally recognized.^{8,34}

Recently, studies have stressed the intrinsic strong tendencies toward the phase sepa-

ration in manganites.^{3,30,35–38} Direct evidences for coexisting localized insulating and delocalized metallic components have been reported from tunnelling spectroscopy, neutron and electron measurements.^{17,39–41} The coexistence between hole-poor and hole-rich phases has been theoretically studied by using exact numerical approaches on small lattices assuming classical Jahn-Teller phonons.^{3,42} Within this approximation the optical properties^{43,44} have been studied but, at low temperatures, in the *FM* phase, the narrow Drude peak, that is experimentally seen,^{28,29} cannot be obtained.

In a recent paper based on a variational approach,⁴⁵ some of us have shown that the quantum nature of the Jahn-Teller phonons and the polaron formation can be important to explain the experimentally observed tendency of manganites to form inhomogeneous magnetic structures near the phase boundaries. Employing the scheme proposed in that work, in a subsequent paper⁴⁶ spectral and optical properties of manganites have been deduced at different temperatures for $x = 0.3$ (around $x = 0.3$ the *CMR* effect is very pronounced in many manganites²). By using the formalism of generalized Matsubara Green's functions^{47–51}, the scattering rate of charges interacting with lattice and spin fluctuations has been determined and used to calculate the optical properties of the system. At low temperatures, in the *FM* phase the system is characterized by two types of optical response: a Drude term and a broad absorption band due respectively to the coherent and incoherent motion of large polarons. At high T the infrared absorption is due to the incoherent small polaron dynamics. Upon cooling, the optical spectra have showed a transfer of spectral weight from high to low energies filling up the low frequency optical gap present in the *PI* phase in agreement with experimental data.^{28,29,52}

In this paper, within the proposed variational approach,^{45,46} we calculate the lattice displacement probability distribution function (*LDPDF*), a quantity measurable by *XAFS* and introduced in order to study the lattice deformations due to the polaron formation.⁵³ It allows to estimate the Debye-Waller (*DW*) factor for several T at $x = 0.3$. Near and within the *PI* phase, the *LDPDF* shows that sites occupied by an electron (Mn^{3+}) are characterized by strong lattice distortions, while sites without conduction electrons (Mn^{4+})

by a vanishing average static displacement. Then we examine the effects of an external magnetic field on the phase diagram, the lattice distortions, the infrared conductivity and the resistivity of the system at $x = 0.3$. Near the phase boundary, the introduction of the field induces a transfer of spectral weight from high to low energies in the conductivity spectra and, consequently, large variations in the resistivity. In this approach, the *CMR* effect is due to the subtle balance between two coexisting phases characterized by different lattice, spin and electronic properties. The comparison between the *DW* factor in presence of the magnetic field and the magnetoresistance ratio points out the correlation between lattice distortions, conductivity and magnetic properties. Finally the isotopic substitution of the oxygen from ^{16}O to ^{18}O is faced, finding that it increases the electron-phonon coupling reducing the Curie temperature T_c . In the vicinity of the *MI* transition, the isotope effect causes large changes of the conductivity, so that it represents another example of the sensitivity of the system to the variation in external parameters.

In Sec. I and II the variational approach and the lattice distortions are respectively discussed; in Sec. III the calculation of the damping of the particle motion and the optical properties are reviewed,⁴⁶ in Sec. IV and V the introduction of an external magnetic field and the isotope effect are respectively examined.

I. VARIATIONAL APPROACH

We adopt a model that takes into account the double-exchange mechanism, the coupling of the e_g electrons to lattice distortions, the super-exchange interaction between neighboring localized t_{2g} electrons and the effects of an external magnetic field \vec{h}_{ext} .^{46,54} The interaction to longitudinal optical phonons derives from the Jahn-Teller effect that splits the e_g double degeneracy. Adopting the single orbital approximation (reasonable in the doping regime where *CMR* occurs⁵⁵), the Hamiltonian reads

$$H = -t \sum_{\langle i,j \rangle} \left(\frac{S_0^{i,j} + 1/2}{2S + 1} \right) c_i^\dagger c_j + \omega_0 \sum_i a_i^\dagger a_i + g\omega_0 \sum_i c_i^\dagger c_i (a_i + a_i^\dagger)$$

$$+ \epsilon \sum_{\langle i,j \rangle} \vec{S}_i \cdot \vec{S}_j - g_s \mu_B \sum_i \vec{h}_{ext} \cdot \vec{S}_i - \mu \sum_i c_i^\dagger c_i. \quad (1)$$

Here t is the transfer integral between nearest neighbor (nn) sites $\langle i, j \rangle$ for electrons occupying e_g orbitals, S is the spin of the t_{2g} core states ($S = 3/2$), $S_0^{i,j}$ is the total spin of the subsystem consisting of the spins localized on a pair of nn sites and the conduction electron, c_i^\dagger (c_i) creates (destroys) an electron with spin parallel to the ionic spin at the i -th site. The first term of the Hamiltonian describes the double-exchange mechanism in the limit where the intra-atomic exchange integral J is far larger than the transfer integral t . In the second term of eq.(1) a_i^\dagger (a_i) is the creation (annihilation) phonon operator at the site i , $\omega_0 = \sqrt{k/M}$ denotes the frequency of the optical phonon mode, with k restoring force per length unit of the local oscillator and M mass of an oxygen atom surrounding the manganese atom. The dimensionless parameter g indicates the strength of the electron-phonon interaction within the Holstein model⁵⁶

$$g = \frac{A}{\omega_0 \sqrt{2M\omega_0}}, \quad (2)$$

where A is the energy per displacement unit due to the coupling of the charge carriers with the lattice. Finally in the Hamiltonian (1) ϵ represents the antiferromagnetic super-exchange coupling between two nn t_{2g} spins, g_s the Lande's electron spin factor ($g_s \simeq 2$), μ_B the Bohr magneton and μ is the chemical potential.

The hopping of electrons is supposed to take place between the equivalent nn sites of a simple cubic lattice separated by the distance $|n - n'| = a$. The units are such that the Planck constant $\hbar = 1$, the Boltzmann constant $k_B = 1$ and the lattice parameter $a = 1$.

We perform two successive canonical transformations to treat the electron-phonon interaction variationally. The first is the variational Lang-Firsov unitary transformation^{57,58}

$$U_1 = \exp \left[-g \sum_j \left(f c_j^\dagger c_j + \Delta \right) \left(a_j - a_j^\dagger \right) \right] \quad (3)$$

where the parameter f measures the degree of the polaronic effects and the parameter Δ denotes a displacement field describing average static lattice distortions. The second Bogoliubov-type transformation⁵⁹

$$U_2 = \exp \left[-\alpha \sum_j \left(a_j^\dagger a_j^\dagger - a_j a_j \right) \right], \quad (4)$$

with α variational parameter, introduces correlations between the emission of successive virtual phonons by the electrons.

The transformed Hamiltonian $\tilde{H} = U_2 U_1 H U_1^{-1} U_2^{-1}$ is difficult to treat exactly, so, in order to obtain a variational free energy,^{45,46} we introduce a test Hamiltonian characterized by electron, phonon and spin degrees of freedom non mutually interacting

$$\begin{aligned} H_{test} = & -t_{eff} \sum_{\langle i,j \rangle} c_i^\dagger c_j + \bar{\omega}_0 \sum_i a_i^\dagger a_i + N\omega_0 \sinh^2(2\alpha) + N\omega_0 g^2 \Delta^2 \\ & -g_s \mu_B \sum_i \vec{h} \cdot \vec{S}_i + (\eta - \mu) \sum_i c_i^\dagger c_i. \end{aligned} \quad (5)$$

The quantity t_{eff} denotes the effective transfer integral

$$t_{eff} = t \left\langle \left(\frac{S_0 + 1/2}{2S + 1} \right) \right\rangle e^{-S_T} \quad (6)$$

where the symbol $\langle \rangle$ indicates a thermal average and the quantity S_T is

$$S_T = g^2 f^2 e^{-4\alpha} (2N_0 + 1), \quad (7)$$

with N_0 the average number of phonons with frequency $\bar{\omega}_0 = \omega_0 \cosh(4\alpha)$. In the test Hamiltonian (5), N is the number of lattice sites, h the sum of the external magnetic field and the molecular magnetic field effective in a cell containing two neighboring sites⁶⁰ and the quantity η

$$\eta = \omega_0 g^2 f (f - 2) + 2\omega_0 g^2 (f - 1) \Delta \quad (8)$$

measures the electronic band shift due to the electron-phonon interaction.

We employ the Bogoliubov inequality in order to derive the variational free energy of the system

$$F \leq F_{test} + \langle \tilde{H} - H_{test} \rangle_t \quad (9)$$

where $\langle \rangle_t$ indicates a thermodynamic average made using the test Hamiltonian, so that the local spin dynamics is studied within a variational mean field theory.⁶¹ The free energy per site becomes

$$\begin{aligned} \frac{F}{N} = & f_{test}^{el} + T \log \left(1 - e^{-\beta \bar{\omega}_0} \right) + \omega_0 \sinh^2(2\alpha) + \omega_0 g^2 (1-f)^2 \rho^2 - T \log \nu_S \\ & \pm \frac{\epsilon}{2} Z S^2 m_S^2 + T \lambda M \end{aligned} \quad (10)$$

where the electron free energy f_{test}^{el} is calculated considering the renormalized band $\bar{\varepsilon}_{\mathbf{k}} = \varepsilon_{\mathbf{k}} + \eta$, where the band dispersion $\varepsilon_{\mathbf{k}}$ is

$$\varepsilon_{\mathbf{k}} = -2t_{eff} [\cos(k_x) + \cos(k_y) + \cos(k_z)]. \quad (11)$$

In eq.(10) β is the inverse of the temperature, ν_S is the partition function of the localized spins, the top and bottom sign of ϵ hold, respectively, for the ferromagnetic and antiferromagnetic solutions of the localized spins and Z indicates the number of nearest neighbors. The quantity λ is a dimensionless variational parameter proportional to the total magnetic field h

$$\lambda = \beta g_s \mu_B S h \quad (12)$$

and $M = B(\lambda)$ is the Brillouin function representing the ratio between the magnetization of the localized spins and the saturation magnetization.

In order to simplify the calculations, we consider a semicircular density of states

$$g(\epsilon) = \left(\frac{2}{\pi W^2} \right) \theta(W - |\epsilon|) \sqrt{W^2 - \epsilon^2} \quad (13)$$

where $W = Zt_{eff}$ is the renormalized band half-width and $\theta(x)$ is the Heaviside function.^{62,63}

In the intermediate electron-phonon coupling regime, the free energy (10) gives rise to a region of coexisting phases characterized by different electron densities ρ_1 and ρ_2 and constituted by large and small polarons, LP and SP , respectively. Thus, near the metal-insulator transition, the system segregates in ferromagnetic and antiferromagnetic or paramagnetic domains of LP and SP .

The variational approach combined with the Maxwell construction allows to determine the fractions of volume of LP and SP . Within the regime of the macroscopic phase separation (PS),^{64,65} it is possible to calculate any thermodynamic property B of the system

by means of the linear combination of the properties B_1 and B_2 characteristic of the single homogeneous phases assuming the respective volume fractions (V_1/V) and (V_2/V) as weights

$$B = \left(\frac{V_1}{V}\right) B_1 + \left(\frac{V_2}{V}\right) B_2. \quad (14)$$

Therefore we assume that in this regime the properties of the system are independent of morphology of coexisting domains neglecting the surface energy cost. In the field of *CMR* manganites, this two-fluid or two-component scenario has been proposed by other workers from a phenomenological point of view.^{8,66} Furthermore, adopting this assumption, in a previous work⁴⁶ the results for spectral properties and infrared absorption have turned out in good agreement with experiments.

In this paper the quantities are calculated taking into account the phase diagram⁴⁶ evaluated by using the following values of the model parameters: $t = 2\omega_0$, $g = 2.8$ and $\epsilon = 0.01t$.

II. LATTICE DISTORTIONS

In this section we deal with the lattice distortions in absence of the external magnetic field.

Within the above-mentioned variational approach, some of us have discussed the Jahn-Teller distortion of the Mn^{3+} ion.⁴⁵ It consists in an axial elongation of two MnO bonds of the MnO_6 octahedra.²³ Above a crossover temperature $T^* < T_c$, there are two distortions of this same type with a different degree of elongation along the axial direction, showing evidence of coexistence of large and small polarons. The average displacement of the site i from the equilibrium position, when one electron is on site i , is in agreement with the experimental data on the separations between local $Mn - O$ bond lengths.⁴⁵

Now we calculate the *LDPDF* $P(X)$, that is more appropriate to make a comparison of the theory with the data obtained by *XAFS* measurements.⁵³ Considering the relevance of the axial elongation, we can confine ourselves to one spatial direction, so

$$P(X) = \langle \delta(X - X_i) \rangle = \frac{1}{2\pi} \int_{-\infty}^{\infty} dq e^{iqX} \langle e^{-iqX_i} \rangle, \quad (15)$$

where $X_i = (a_i + a_i^\dagger)/\sqrt{2M\omega_0}$ is the displacement operator at the site i along a reference axis. It has been evaluated performing the two canonical transformations (3,4) and making the decoupling⁴⁶ in the electron and phonon terms through the introduction of H_{test} (5). We get

$$P(X) = \frac{1}{\sqrt{\pi}l} \left[\rho e^{-(x-b)^2/l^2} + (1-\rho) e^{-(x-c)^2/l^2} \right] \quad (16)$$

where ρ is the electron density, $l = \sqrt{\frac{(2N_0+1)e^{4\alpha}}{M\omega_0}}$, $b = g\sqrt{\frac{2}{M\omega_0}}(\Delta + f)$ and $c = g\sqrt{\frac{2}{M\omega_0}}\Delta$. We obtain two terms: the first is due to the average occupation of the site i and involves directly the polaronic distortion controlled by the variational parameter f , the second is due to the remaining configurations without electron on the site i and it is related to the average lattice displacement $\Delta = \rho(1-f)$. In Fig. 1(a) we report the distribution $P(X)$ for different temperatures at $x = 0.3$. In the regime of coexisting phases $LDPDF$ takes contribution from both $LP-FM$ and $SP-PI$ distributions by means of the eq.(14). The $LP-FM$ phase is characterized by a single-peak $LDPDF$ centred about the average lattice displacement Δ (here f is smaller than Δ). With increasing temperature, the spreading of $P(X)$ signals the PS regime and near T_c two well-defined peaks appear giving a bimodal $LDPDF$. Near and in the insulating state, occupied sites (Mn^{3+}) have strong distortions while non-occupied sites (Mn^{4+}) are characterized by an average static displacement Δ equal to zero.^{19,21}

We have derived the mean-square deviation of this distribution $\Delta x^2 = \langle x^2 \rangle - \langle x \rangle^2$ that provides the DW factor (see in Fig. 1(b) DW as a function of T at $x = 0.3$). The DW factor increases rapidly with temperature near T_c in agreement with experimental data.^{20,22,67}

III. DAMPING AND OPTICAL PROPERTIES

In this section we briefly review the calculations of the scattering rate and the infrared absorption due to lattice distortions and spin fluctuations.⁴⁶

Retaining only the dominant autocorrelation terms at the second step of iteration^{47–51}, the self-energy $\Sigma^{(2)}(\mathbf{k}, i\omega_n)$ and the scattering rate

$$\Gamma(\mathbf{k}) = \tilde{\Gamma}(\mathbf{k}, \omega = \xi_{\mathbf{k}}) = -2\Im\Sigma_{ret}^{(2)}(\mathbf{k}, \omega = \xi_{\mathbf{k}}) \quad (17)$$

are derived. Making the expansion into the series of multiphonon processes, the scattering rate is expressed as

$$\Gamma(\mathbf{k}) = \Gamma(\xi_{\mathbf{k}}) = \Gamma_{1-phon}(\xi_{\mathbf{k}}) + \Gamma_{multi-phon}(\xi_{\mathbf{k}}) + \Gamma_{Spin-Fluct}(\xi_{\mathbf{k}}) \quad (18)$$

where Γ_{1-phon} is the contribution due to single phonon processes, $\Gamma_{multi-phon}$ represents the scattering rate by multiphonon processes and $\Gamma_{Spin-Fluct}$ denotes the damping term by spin fluctuations. At low T , in the LP phase, single phonon emission and absorption represent the main mechanism of scattering. Furthermore, at higher temperatures the damping due to spin fluctuations is effective in the energy range around the chemical potential μ .

The scattering rate turns out fundamental to derive the infrared absorption of the system. The real part of the conductivity is obtained by the current-current correlation function

$$\Re\sigma_{\alpha,\alpha}(\omega) = -\frac{\Im\Pi_{\alpha,\alpha}^{ret}(\omega)}{\omega} \quad (19)$$

where the current operator j_{α} suitable for the Hamiltonian (1) is

$$j_{\alpha} = ite \sum_{i,\delta} \delta_{\hat{\alpha}} \left(\frac{S_0^{i+\delta\hat{\alpha},i} + 1/2}{2S+1} \right) c_{i+\delta\hat{\alpha}}^{\dagger} c_i. \quad (20)$$

The conductivity can be expressed as sum of two terms

$$\Re\sigma_{\alpha,\alpha}(\omega) = -\frac{\Im \left[\Pi_{\alpha,\alpha}^{ret(1)}(\omega) + \Pi_{\alpha,\alpha}^{ret(2)}(\omega) \right]}{\omega} = \Re\sigma_{\alpha,\alpha}^{(band)}(\omega) + \Re\sigma_{\alpha,\alpha}^{(incoh)}(\omega). \quad (21)$$

The first term $\Re\sigma_{\alpha,\alpha}^{(band)}$ represents the band conductivity because the absorption is not accompanied by processes changing the number of phonons. On the other hand, the second term marked by the apex “incoherent” in eq. (21) derives from inelastic scattering processes of emission and absorption of phonons. The band conductivity is derived as

$$\Re\sigma_{\alpha,\alpha}^{(band)}(\omega) = \left(\frac{4e^2 t^2}{\omega} \right) e^{-2S_T} \left\langle \left(\frac{S_0 + 1/2}{2S+1} \right) \right\rangle^2 \int_{-\infty}^{+\infty} d\xi [n_F(\xi - \omega) - n_F(\xi)] \tilde{C}(\xi, \omega) h(\xi) \quad (22)$$

where $\tilde{C}(\xi, \omega)$ is

$$\tilde{C}(\xi, \omega) = \frac{\Gamma(\xi)}{\Gamma^2(\xi) + \omega^2} \quad (23)$$

and $h(\xi)$ reads

$$h(\xi) = \left(\frac{1}{N}\right) \sum_{\mathbf{k}} \sin^2(k_{\alpha}) \delta(\xi - \xi_{\mathbf{k}}). \quad (24)$$

The latter term of the conductivity becomes

$$\begin{aligned} \Re \sigma_{\alpha, \alpha}^{(incoh)}(\omega) &= \left(\frac{2e^2 t^2}{\omega}\right) e^{-2S_T} \left\langle \left(\frac{S_0 + 1/2}{2S + 1}\right)^2 \right\rangle \int_{-\infty}^{+\infty} d\xi \int_{-\infty}^{+\infty} d\xi_1 g(\xi) g(\xi_1) R(\xi, \xi_1, \omega) + \\ &\quad \left(\frac{2e^2 t^2}{\omega}\right) e^{-2S_T} \left[I_0(z) \left\langle \left(\frac{S_0 + 1/2}{2S + 1}\right)^2 \right\rangle - \left\langle \left(\frac{S_0 + 1/2}{2S + 1}\right) \right\rangle^2 \right] \times \\ &\quad \times \int_{-\infty}^{+\infty} d\xi \int_{-\infty}^{+\infty} d\xi_1 g(\xi) g(\xi_1) [n_F(\xi - \omega) - n_F(\xi)] C(\xi, \xi_1, \omega) \end{aligned} \quad (25)$$

where $g(\xi)$ is the density of states (13) and the function $R(\xi, \xi_1, \omega)$ is given by

$$R(\xi, \xi_1, \omega) = 2 \sum_{l=1}^{+\infty} I_l(z) \sinh\left(\frac{\beta \bar{\omega}_0 l}{2}\right) [J_l(\xi, \xi_1, \omega) + H_l(\xi, \xi_1, \omega)]. \quad (26)$$

We notice that $J_l(\xi, \xi_1, \omega)$

$$J_l(\xi, \xi_1, \omega) = C(\xi, \xi_1, \omega + l\bar{\omega}_0) [n_F(\xi - l\bar{\omega}_0 - \omega) - n_F(\xi - l\bar{\omega}_0)] [N_0(l\bar{\omega}_0) + n_F(\xi)] \quad (27)$$

and $H_l(\xi, \xi_1, \omega)$

$$H_l(\xi, \xi_1, \omega) = C(\xi, \xi_1, \omega - l\bar{\omega}_0) [n_F(\xi + l\bar{\omega}_0 - \omega) - n_F(\xi + l\bar{\omega}_0)] [N_0(l\bar{\omega}_0) + 1 - n_F(\xi)] \quad (28)$$

describe phonon absorption and emission processes, respectively.

In the limit of high temperatures ($T > 0.39\omega_0$) and for SP excitations, the incoherent absorption is prevalent. In this case the conductivity consists of a sum of narrow Lorentzian functions centred on the points $n\omega_0$ respectively.⁶⁸ A derivation suitable for high temperatures can be performed and gives⁶⁹

$$\begin{aligned} \Re \sigma_{\alpha, \alpha}(\omega) &= \\ &\left(\frac{e^2 t^2}{\omega}\right) \left\langle \left(\frac{S_0 + 1/2}{2S + 1}\right)^2 \right\rangle \sqrt{\frac{\pi\beta}{\bar{z}}} \left\{ \exp\left[-\frac{\beta}{4\bar{z}}(\omega - \bar{z})^2\right] - \exp\left[-\frac{\beta}{4\bar{z}}(\omega + \bar{z})^2\right] \right\} \rho(1 - \rho) \end{aligned} \quad (29)$$

where ρ is the electron concentration.

The conductivity $\sigma_{\alpha,\alpha}$ is given by eq.(21) and eq.(29) in $LP-FM$ and $SP-PI$ phase, respectively. In the regime of coexisting phases, the two preceding conductivities are combined by means of the eq.(14).

At low temperatures, in the FM phase the system shows two types of optical response: a Drude term and a broad absorption band due respectively to the coherent and incoherent motion of large polarons. With increasing T , the optical spectra are characterized by a transfer of spectral weight from low to high energies. At high T the infrared absorption consists in a band peaked approximatively around the energy $2g^2\omega_0$ and is due to the incoherent SP dynamics.^{30,31} The experimental data can be fitted reasonably well with the LP and SP spectra below 0.8 eV.^{28,29,52} Indeed we note that for high frequencies the effects due to the exchange-split bands and to the local Coulomb repulsion should be included.⁷⁰ Thus the results can be considered meaningful for frequencies up to the absorption peak of the SP band.

IV. EFFECTS OF AN EXTERNAL MAGNETIC FIELD

In this section we discuss the effects of an external magnetic field on the optical properties of the system at $x = 0.3$.

We first note that a unit of magnetic field h_0 can be fixed as

$$h_0 = \frac{\omega_0}{g_s\mu_B S}. \quad (30)$$

If we choose for ω_0 a reasonable value of 50meV, this unit is huge: in fact h_0 is of the order of 300 T. For realistic values of the magnetic fields the new energy scale $g_s\mu_B Sh_0$ is small when compared with ω_0 . However in presence of an external magnetic field the phase diagram shows the tendency for $LP-FM$ and $FM-PI$ regions to grow. By introducing an external magnetic field (see Fig. 2), the magnetization does not vanish at T_c , the transition temperature in absence of the field, showing the behavior of a first order transition.^{35,71} Thus,

in the vicinity of the transition temperature, the subtle balance between the two coexisting phases can be readily influenced by varying the magnetic field.

The increase of the coherent motion due to the introduction of the external field is clearly shown in the calculated conductivity. We limit ourselves to the diagonal component. In Fig. 3(a) we can notice the rise of the Drude term with increasing the magnetic field, while in Fig. 3(b) the small-polaron absorption band is suppressed. This behavior is more pronounced at higher temperatures (see Fig. 4 for $T = 0.96T_c$). At T_c the introduction of the magnetic field is able to fill up the low frequency optical gap present in the high-temperature phase (Fig. 5). Hence the magnetic field induces the transfer of spectral weight from high to low energies near the phase boundary.⁷²

The introduction of the magnetic field has dramatic consequences on the resistivity $\rho = 1/\sigma_{\alpha,\alpha}$ near T_c , where $\sigma_{\alpha,\alpha}$ results from the conductivity $\sigma_{\alpha,\alpha}(\omega)$ in the limit $\omega \rightarrow 0$ (Fig. 6). We obtain two different behaviors: metallic ($d\rho/dT > 0$) and insulating ($d\rho/dT < 0$) emphasizing in logarithmic scale the behavior of activated resistivity characteristic of a *SP* phase for $T > T_c$.^{9,10} The magnetic field shifts the peak of the resistivity at higher temperatures. Since the *PS* regime is characterized by a rapid increase of the resistivity,⁴⁶ at T_c a large difference between resistivities at different magnetic fields occurs. The magnetoresistance ratio (see in Fig. 7(a) *MR* in percent)

$$MR(h) = \frac{[\rho(h=0) - \rho(h)]}{\rho(h)} \quad (31)$$

assumes large values at the transition temperature, so that the effect of the magnetic field is dramatically amplified near T_c .^{1,9} Therefore, the *CMR* effect and, in general, the high sensitivity of the system to external parameters are due to the subtle balance between *LP-FM* and *SP-PI* phases characterized by different lattice, spin and charge properties.

We have calculated the effect of the applied magnetic field on the *DW* factor. In Fig. 7(b) we report $\Delta(DW)$, the relative variation of the *DW* factors obtained without and with the external field, in order to make a comparison with the magnetoresistance ratio.^{73,74} The quantity $\Delta(DW)$ shows a well defined peak around the transition temperature, indicating

that the application of the magnetic field reduces the polaronic distortions. The two quantities, MR and $\Delta(DW)$ in Fig. 7, are both peaked around T_c showing the existence of a strong correlation between lattice distortions, conductivity and magnetic properties.²²

V. ISOTOPE EFFECT

In this section we deal with the isotope effect in the *CMR* regime at $x = 0.3$. In particular we calculate the effects of isotope substitution on the infrared spectra.

The isotopic substitution of the oxygen from ^{16}O to ^{18}O changes the values of ω_0 and g to $\omega_0^* = \omega_0\sqrt{M/M^*}$ and $g^* = g(M^*/M)^{1/4}$ respectively, where M^* is the mass of ^{18}O . The coupling parameter $\lambda = g^2\omega_0/6t$ is clearly unchanged.

In Fig. 8 the phase diagram for ^{18}O is presented and compared with that of ^{16}O . It is qualitatively altered with respect to the phase diagram of ^{16}O showing a reduction of the *FM* regions.^{32,33,75–79} The heavier ion mass of ^{18}O reduces the effective transfer integral t_{eff} (see eq. (6)), so the region of coexisting phases and in particular the Curie temperature T_c decrease. Indeed, in the limit where the intra-atomic exchange integral J is far larger than the bare transfer integral t , $T_c \propto t_{eff}$.^{7,60} In the inset of Fig. 8, T_c^* , the Curie temperature for ^{18}O , is reported along with T_c , the Curie temperature for ^{16}O . We have evaluated the oxygen-isotope exponent $\alpha_0 = -\Delta\ln T_c / \Delta\ln M = -\frac{(T_c^* - T_c)}{T_c} \frac{M}{(M^* - M)}$, making a comparison with experimental values.³³ We find the decreasing behavior of α_0 with increasing the hole doping x (Fig. 9).

Near T_c we have calculated the optical conductivity for the two isotopes (Fig.10). While the ^{16}O system is in the *PS* regime, ^{18}O system is in the insulating phase. In the first case the optical response still shows the Drude term, for ^{18}O only the small-polaron band at high frequency is present. Again this causes large changes in the conductivity of the system. Therefore the isotope effect represents another example of the sensitivity to the variation in external parameters.

VI. CONCLUSIONS

We have discussed the effects of an external magnetic field and of the oxygen isotopic substitution on the infrared absorption spectra for $x = 0.3$ mainly near the phase boundary. Furthermore we have dealt with the lattice effects and the DW factor without and with the magnetic field.

First we have focused our attention on *LDPDF* finding that, near and in the *PI* phase, only the sites occupied by an electron show strong lattice distortions and that the DW factor increases rapidly with temperature near T_c in agreement with *XAFS* measurements.^{19–22}

Then we have examined the consequences of an external magnetic field on the infrared absorption spectra at $x = 0.3$ stressing that, near the phase boundary, the application of the field induces a transfer of spectral weight from high to low energies⁷² and evaluating the *CMR* ratio. In our scheme, the found *CMR* is due to the subtle balance between coexisting phases characterized by different lattice, spin and electronic properties. The relation between the *CMR* ratio and the variation of the DW factor in presence of the magnetic field has pointed out the correlation that involves lattice distortions, conductivity and magnetic properties.

Finally, within our approach, the oxygen isotope effect has been explained by the enhanced electron-phonon coupling that induces a reduction of the *FM* phases. In the vicinity of the *MI* transition the isotope substitution induces large changes in the optical response and in the resistivity in agreement with experimental data.^{32,33,75,76}

We believe that the strong sensibility of the infrared absorption with respect to the magnetic field and isotopic substitution could be used to test the validity of the *PS* scenario adopted in this paper. Indeed the experimental study of the infrared absorption is well established and it could be able to observe the effects discussed above.

In our work, near the *MI* transition, the interplay of the electron-phonon interaction and the magnetic effects gives rise to a charge-density instability that takes into account experimental evidences for coexisting localized insulating and delocalized metallic

components.^{36–41,66} We have assumed that the scales of the inhomogeneities are much larger than the inter-particle distance and that the term arising from the mixing energy of the two coexisting phases and including the surface energy cost is not able to change qualitatively the behavior of the macroscopic quantities discussed. We have exploited a macroscopic *PS* scenario where the coexisting fractions of volume are determined by the variational procedure and the Maxwell construction. This approach to manganites provides results consistent with experimental measurements^{45,46} and an explanation of the strong sensitivity of the system to external parameters.

FIGURE CAPTIONS

- F1 (a) The distribution function of the atomic displacement (in units of $\sqrt{M\omega_0/2}$) at $x = 0.3$ as a function of the displacement coordinate X (in units of $2/\sqrt{M\omega_0}$ different from the length unit introduced above, the lattice constant a).
- (b) The Debye-Waller factor (in units of $2/M\omega_0$) at $x = 0.3$ as a function of the temperature.
- F2 The magnetization (in units of saturation magnetization M_S) as a function of the temperature for two different magnetic fields (in units of h_0).
- F3 (a)-(b) The diagonal conductivity at $T = 0.9 T_c$ at different ranges of the frequency ω for several magnetic fields (in units of h_0). The conductivities are expressed in units of $e^2c/m\omega_0$, with c hole concentration and $m = 1/2t$.
- F4 (a)-(b) The diagonal conductivity (in units of $e^2c/m\omega_0$, with c hole concentration and $m = 1/2t$) at $T = 0.96 T_c$ at different ranges of the frequency ω for several magnetic fields (in units of h_0).
- F5 The diagonal conductivity up to $18 \omega_0$ at $T = 1.02 T_c$ for different magnetic fields (in units of h_0). The conductivity is expressed in units of $e^2c/m\omega_0$, with c hole concentration and $m = 1/2t$.

- F6 The inverse of the diagonal conductivity as a function of the temperature at different magnetic fields (in units of h_0) (we have used $\omega_0 = 50 \text{ meV}$ and the lattice constant $a = 0.4 \text{ nm}$).
- F7 (a) The magnetoresistance ratio at a fixed magnetic field (in units of h_0) as a function of the temperature.
- (b) The relative variation of the Debye-Waller factor at a fixed magnetic field (in units of h_0) as a function of the temperature.
- F8 The phase diagram for the two different oxygen isotopes (^{16}O dashed line, ^{18}O dotted line). *PI* means Paramagnetic Insulator, *FM* Ferromagnetic Metal and *AFI* AntiFerromagnetic Insulator. The areas *PI* + *FM* and *AFI* + *FM* indicate regions where localized (*PI* or *AFI*) and delocalized (*FM*) phases coexist. In the inset the ferromagnetic transition temperatures as a function of the hole doping (T_c dashed line for ^{16}O and T_c^* dotted line for ^{18}O). The temperatures are expressed in units of ω_0 and the model parameters are $t = 2\omega_0$, $g = 2.8$ ($\lambda = 0.65$ for both isotopes) and $\epsilon = 0.01t$.
- F9 The oxygen-isotope exponent α_0 (circles) compared to the experimental exponent (diamonds) deduced by Ref. 33 as a function of the hole doping.
- F10 The conductivity at $T = 0.97 T_c$ up to $19 \omega_0$ for ^{16}O and ^{18}O . The conductivities are expressed in units of $e^2 c / m \omega_0$, with c hole concentration and $m = 1/2t$.

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